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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report covers the period from May 1, 1985 to July 31, 1988. A study was made of the structural features and thermodynamic aspects of a primitive model electric double layer, that is, a system of charged hard spheres of arbitrary diameters embedded in a dielectric continuum, next to a uniformly charged planar interface. This study has been conducted in collaboration with Dr. C. W. Outhwaite of the Department of Applied and Computational Mathematics, University of Sheffield, Sheffield, United Kingdom. This report contained the results of this study.		

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→ Key words

MODIFIED POISSON-BOLTZMANN EQUATION IN THE ELECTRIC
DOUBLE LAYER THEORY FOR AN ELECTROLYTE WITH SIZE
ASYMMETRIC IONS

L.B.Bhuiyan and C.W.Outhwaite

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FINAL REPORT

This report covers the period from May 1, 1985 to July 31, 1988. We have looked into the structural features and thermodynamic aspects of a primitive model electric double layer, that is, a system of charged hard spheres of arbitrary diameters embedded in a dielectric continuum, next to a uniformly charged planar interface. This study has been conducted in collaboration with Dr. C.W. Outhwaite of the Department of Applied and Computational Mathematics, University of Sheffield, Sheffield, United Kingdom.

The so-called restricted primitive model (RPM) double layer, where the ions have a common diameter has been the subject of numerous theoretical (statistical mechanical) and numerical (Monte-Carlo (MC)) treatments over the last decade, and a fairly complete description of this system is available. Our idea was to relax the ionic size-asymmetry restriction of the RPM and thereby study the structural changes occurring in the interface system, now with a more realistic electrolyte. We have treated this primitive model double layer using a Modified Poisson-Boltzmann (MPB) theory, the motivation being the theory's enormous success in predicting the properties of bulk electrolytes and the RPM double layer. In essence, the MPB approach seeks to correct the approximations inherent in the classical Poisson-Boltzmann theory, the two important ones being the neglect of the fluctuation potential and the exclusion volume effect of the ions.

The MPB theory results in a rather complicated non-linear equation. In order to better understand its implications, the

corresponding linearized equation was studied. We found that as in the earlier MPB studies of the RPM double layer, the potential and the ion-density profiles undergo a transition from a monotonic to a non-monotonic behaviour beyond a critical concentration of the electrolyte solution. This critical concentration, in general, depends in a complicated way on the ionic diameter ratio and ionic valences. The full non-linear equation (for no imaging) was solved numerically using a quasi-linearization iterative technique. Detailed results have been obtained for a symmetric 1:1 valence electrolyte. A striking feature of the results is the appearance of a finite non-zero potential of zero charge (PZC) (on the wall). This is not seen in the corresponding RPM case, and indicates that a charge separation is occurring at the interface. Another important effect of ionic size asymmetry is the unsymmetrical nature of the differential capacity curves. The latter two features are routinely observed in experiments. Results have been published in the literature in the Journal of Chemical Physics and in the Proceedings of the 10th Nathiagali International Summer College, held in Nathiagali, Pakistan.

We used a two-term fluctuation potential solution in the derivation of the MPB equation. We have noticed that this technique applied to the equi-sized ion case has the welcome effect that the ionic-density profiles no longer have discontinuities in their slopes. We did some calculations for this case both for symmetrical and asymmetrical valency electrolytes, and also considered imaging, for example, use of a metallic wall. The results, when compared to the earlier MPB5 theory of the RPM double layer vis-a-vis available MC results, seem mixed, being superior to MPB5 in some cases and inferior

to MPB5 in some other cases. Further improvement of the MPB theory for the RPM double layer was also considered based on a more complete solution of the fluctuation potential problem near the wall. The solution is developed using the Fourier-Bessel techniques and has the feature that the ion-ion pair correlations in the inhomogeneous region next to the wall decay as r^{-3} parallel to the wall. This r^{-3} dependence is an exact condition (sum rule) on the pair correlations. However, to obtain detailed solutions for the potential and the density profiles considerable and involved numerical work would be required.

We have also considered the thermodynamic consistency of the MPB equation for the double layer. From the contact values (at the wall) of the ion-density profiles for zero wall charge, it is possible to predict the bulk osmotic coefficients and the activity coefficients. The MPB results for these for the RPM system have been compared to those from other theories of the double layer such as the hypernetted chain approximation (HNC/HNC), the MPB and the HNC theories of the bulk electrolyte, and the MC simulations. We found that (a) overall for monovalent electrolyte/salts the MPB theory of the interface is satisfactory, being of comparable accuracy to the HNC/HNC theory, and, (b) the approximations involved in the MPB approach to the double layer do not lead to serious violations of the thermodynamic consistency of the system. A paper on these calculations has been published in the Journal of Physical Chemistry.

We have also reported to the literature the MPB values of the potential drop across the diffuse double layer containing the RPM electrolyte using the MC simulation parameters for the model. These

calculations use a one-term fluctuation potential. We note that the theory satisfies the contact value theorem (relating the contact values of the singlet wall-ion distribution functions to the bulk fluid pressure and the surface electric field) fairly accurately for 1:1 valency electrolytes and satisfactorily for higher valency systems. An article on this has been published in the Journal of Chemical Physics.

We next looked at the civilized model electric double layer consisting of a mixture of hard sphere ions and hard sphere dipoles next to a uniformly charged planar interface. This is a simple non-trivial model that considers the 'discreteness of the solvent' and treats the solute (hard sphere ions) and the solvent (hard sphere dipoles) on an equal footing. Although still simplified, the model represents a step closer to reality than the primitive model where all solvent structure is neglected, the solvent, as mentioned earlier, being a dielectric continuum. Our ultimate aim is to explore the MPB for this civilized model. To this end, as an initial step, we have employed the mean field theory (i.e. the Poisson-Boltzmann theory) to the system since knowledge of the ramifications of the PB theory is essential to the development of the MPB theory. Further, under certain limiting conditions the MPB theory reduces to the PB theory so that the latter serves as a check. Also, in the iterative solutions to the MPB equation, results of the PB equation are often a very good initial guess. The mean field theory was earlier applied to this model interface by Outhwaite (Chem. Phys. Letts.(1980), Can. J. Chem.(1981)), who showed using the linearized theory that the results for the differential (and integral) capacitances can be derived very

simply, and that the capacitances have the same structural features as those from a more involved derivation using a more complicated theory such as the mean spherical approximation(MSA).

Various cases have been treated. Initially we considered the situation where all the ions have the same radii a_I and the dipoles (one species for simplicity) have the radii a_D . For both $a_I > a_D$ and $a_I < a_D$ solutions were obtained with dipole terms linearized and for the non-linear equation. Although analytic solutions are possible for the former theory (for $a_I < a_D$ the solutions involve elliptic functions), the latter case can only be treated numerically. The important findings were the non-linear dependence of the capacitances (both integral and differential) on the surface charge density. The completely linear mean field theory as also the MSA fail to show this result. Further, for $a_I < a_D$, the predictions from the dipole linear theory are very close to those from the full non-linear theory. This is reasonable since in the region very close to the wall non-linear charge screening is the most important when $a_I < a_D$. A paper on these was presented at the 171st meeting of the Electrochemical Society held in Philadelphia.

We next considered the situation where the ionic radii are a_i, a_j (for the cations and the anions respectively, for a single electrolyte) the dipole radii being a_d . The three situations $a_d < a_i < a_j$, $a_i < a_d < a_j$ and $a_i < a_j < a_d$ were all examined in details for the completely linear theory and the dipole linear theory. Analytical solutions are possible in principle, however, numerical techniques are more convenient for some cases where the dipole terms are linearized. The principal results are (a) the fully linear theory gives a

capacitance (both integral and differential) that is independent of the surface charge as in the equi-sized ion case, (b) asymmetric capacitance versus surface charge density curves for the dipole linearized theory. This is observed experimentally., (c) non-zero potentials of zero charge(PZC). The PZC versus $c^{1/2}$ (c is the salt concentration) curves are, as expected, very similar for the two theories at lower concentrations with differences occurring at higher concentrations, and, (d) Parsons-Zobel curves (plots of inverse differential capacitance versus inverse of the diffuse layer capacitance given by the Modified Gouy-Chapman theory) that reproduce qualitatively the corresponding experimental results. However, the PB theory is flawed through poor value of the permittivity of the solvent and the lack of structure in the singlet distribution functions and the potential profiles. A paper on these results has been accepted for publication by the Journal of Physical Chemistry.

The following papers have been published/accepted for publication.

1. "A Modified Poisson-Boltzmann Equation in Electric Double Layer Theory for a Primitive Model Electrolyte with Size-Asymmetric Ions", by C.W.Outhwaite and L.B.Bhuiyan; J. Chem. Phys. 84, 3461(1986)
2. "Modified Poisson-Boltzmann theory in the Electric Double Layer Containing Size-Asymmetric Ions", by L.B.Bhuiyan and C.W.Outhwaite; in Contributed Seminars, 10th International Nathiagali Summer College, 1985, I.E.Qureshi, A.Sadiq and K.Rashid eds., p. 239
3. "The MPB5 Diffuse Layer Potential Drop", by C.W.Outhwaite and L.B. Bhuiyan; J. Chem. Phys. 85, 4206(1986)
4. "The Thermodynamic Consistency of the Modified Poisson-Boltzmann Equation in the Electric Double Layer", by D.Bratko, L.B.Bhuiyan and C.W.Outhwaite, J. Phys. Chem. 90, 6248(1986)
5. "A Mean Field Analysis of an Ion-Dipole Mixture next to a Plane Charged Wall", by C.W.Outhwaite and L.B.Bhuiyan; Extended

Abstracts, The Electrochemical Society, 87-1, 609(1987)

6. "A Mean Field Analysis of an Ion-Dipole Mixture next to a Plane Charged Wall", by L.B.Bhuiyan and C.W.Outhwaite; J. Phys. Chem. (in the press)

During the reporting period LBB presented seminars on the research findings at the University of Puerto Rico (Rio Piedras campus), the Interamerican University of Puerto Rico (San German campus), 10th International Nathiagali Summer College, Pakistan, E. Kardelj University, Yugoslavia, Chalmers Institute of Technology, Sweden, the University of Dhaka, Bangladesh and Jadavpur University, India, while CWO presented the paper at the 171st meeting of the Electrochemical Society held in Philadelphia. LBB had an interesting and fruitful trip to the U.S.Army Electronics Technology and Devices Laboratory, Power Sources Division at Fort Monmouth, New Jersey, where he presented a seminar entitled "The Modified Poisson-Boltzmann Approach to the Electric Double Layer Problem". He is grateful to Dr. Robert Shaw of the ARO for making the trip possible, and would like to thank Drs. S.Gilman and M.Salomon of ETDL Power Sources Division for their hospitality during the visit.